MONITORING WATER VAPOUR PENETRATION USING A CONTACTLESS TECHNIQUE

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ABSTRACT: Some layers of thin film photovoltaic modules maybe critically sensitive to moisture. In this study we present a new tool for monitoring the effect of moisture using a particular Transparent Conductive Oxide (TCO) as a sensor. The moisture content of the encapsulant was determined by Fourier Transform Infra Red (FTIR) spectroscopic measurements. The TCO resistivity was measured using an inductive method. The different spectroscopic results show that the diffusion of water vapour in the encapsulant used in this study is in good agreement with Fick's law and correlate well with the increase of resistivity of the TCO. However, the transport measurements bring evidence for a degradation of the TCO resistivity undetectable by conventional FTIR measurements.
Keywords: moisture, diffusion, monitoring, TCO

1 INTRODUCTION

Water vapour diffusion in PV modules can drastically affects several constituents, such as front and back contacts, adhesion of polymers, etc. [1-3].

In this study we aimed to correlate the moisture content in the polymer and the degradation of the resistivity of the transparent conductive oxide (TCO). For this purpose, a dedicated TCO made of boron doped zinc oxide has been used as an indicator of moisture ingress inside a laminate. This TCO is more moisture sensitive than commercial ones; therefore its degradation occurs faster in presence of moisture. The moisture affects the resistivity of the TCO due to the water vapour absorption at the grain boundaries which reduces the inter-grain mobility of the free carriers [4,5].

We used as a typical sample configuration: a sheet of polymer between a TCO glass coated and a back glass, laminated together. We measured the evolution of the sheet resistivity during exposure in damp heat chamber according to the norm IEC 61646 (85°C and 85% relative humidity). For this purpose, we used an inductive method. This method is contactless and permits to avoid any preferential pathway of water vapour along contact wires. Moreover, this technique allows measuring the sheet resistivity with a spatial resolution of the order of a couple of centimetres. In addition we also monitored the evolution of the optical transmission in the Near Infra Red domain.

The FTIR measurements have been fitted to a Fickian diffusion model which gave good results. For the change in resistivity as a function of moisture exposure, a doping dependant model is under investigation. One must be aware that in this study, the diffusion may depend not only on the polymer characteristics (bulk properties) but also on the properties of the stack (adhesion). In principle, a careful analysis of a more complete set of data would allow to distinguish between the diffusion in the polymer, at the interfaces or, maybe, in the TCO.

Resistivity measurements allow qualifying non transparent samples, for example, with white paint coating.

2 EXPERIMENTAL

2.1 Sample design

A low-doped zinc oxide layer of around 2 μm thick was deposited on 4 mm thick glass (100x250 mm^2 and 200x250mm^2) by Low Pressure Chemical Vapour Deposition process (see **Figure 1**).

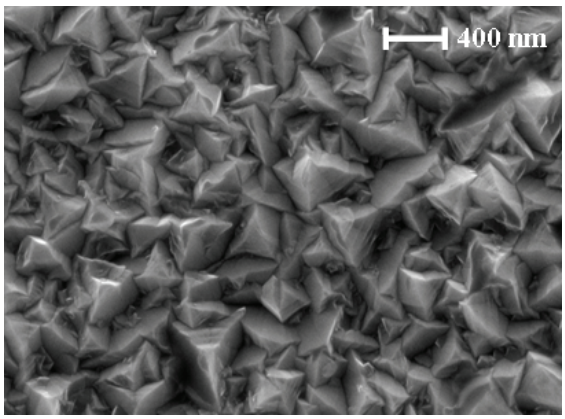

Figure 1: SEM micrograph of in-house LP-CVD ZnO.

The ZnO was removed at edges (0, 1, 2 and 3 cm), but also on some spots in order to avoid scattering and absorption of light in ZnO. A dielectric white reflective paint was applied on the ZnO layer of some of the samples, in order to study the protective effect of the paint on the TCO. All samples were encapsulated with a commercial Poly Vinyl Butyral in a R&D vacuum laminator S1815 from 3S. The 100*250mm^2 samples were sealed with butyl and aluminium tape on three edges, the open edge being 100mm wide. The 200*200mm^2 samples were not sealed.

2.2 Measurements

Resistivity measurements are performed on each sample using a Wafer Lifetime Tester from Sinton Consulting [6]. It consists in a coil, embedded in a RLC resonant tank circuit, which produces a high frequency magnetic field. When a conducting body is placed in this time varying magnetic field, Eddy currents start flowing

due to the induced electric field. In our samples, the Eddy currents circulate in the ZnO layer and, as a result, modify the effective inductance and resistance of the RLC resonant circuit. This is detected as amplitude and phase change in the tank circuit from which on can infer a sheet resistance value for the TCO layer. The size of the coil of about 20mm of diameter defines the area to be measured on the samples. Resistivity is measured on 8 points and 7 points for the 100*250mm^2 and 200*200mm^2 samples, respectively.

FTIR spectra are recorded for non-painted samples, on a Vertex 70 from Bruker Optics. Spectra are recorded from 350 to 7500 cm^{-1} (from 1.4 to 28 microns); the interesting region being between 5000 to 6100 cm^{-1}. The spectra are directly converted from transmission to absorption (A=-log(T)). 11 points are measured for each sample.

Those measurements have been taken initially and after each aging cycles (~40h), at 85°C and 85% Relative Humidity.

3 RESULTS

3.1 Visual

During aging, no yellowing and delamination of the polymer have been visible. The paint seems to peel at some places, where water vapour content is high like near the edges.

3.2 FTIR spectra

Organic bonds are excited by the infrared light. In our stack, the characteristic peaks appear between 3500 and 6100 cm^{-1}. PVB has a combination of frequencies which correspond to carbon-hydrogen bond, taken here as the reference peak. A combination of the asymmetric stretching and bending of water appeared at 5200cm^{-1} [7]. During aging in damp heat chamber, the water peak area increased whereas the CH_x peak stayed unchanged since absorption is proportional to the concentration of the corresponding molecule (see **Figure 2**).

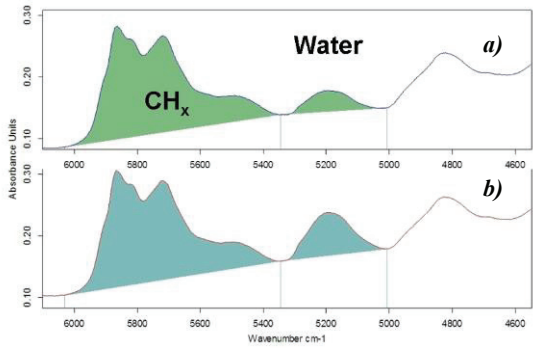

Figure 2 : Detail of absorption spectra of the same point at 0h (a) and 234h (b) in damp heat chamber. The characteristic peak of the polymer appeared between 6000 and 5300 cm^{-1} and the water peak appeared between 5300 and 5000 cm^{-1}.

The peaks are integrated and the water peak area is normalized with the CH_x area. This FTIR ratio is plotted for each samples, as a function of distance x from open edge (see **Figure 3**) and as a function of time t in the climate chamber (see **Figure 4**). Cycles of 40h are short enough to see water diffusing gradually in the laminate. A complementary measurement would be necessary to know the quantitative relation between absorption peak area and molar concentration.

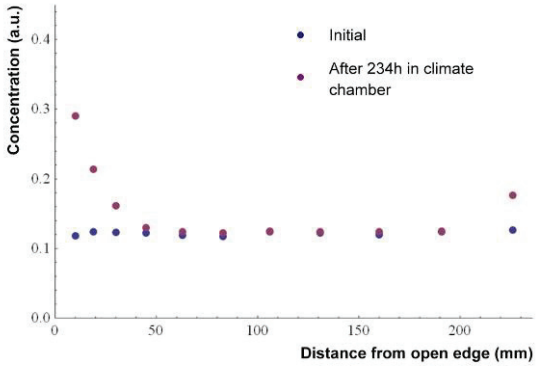

Figure 3: Example of FTIR ratio plotted as a function of distance from open edge, after lamination and after 234h in climate chamber.

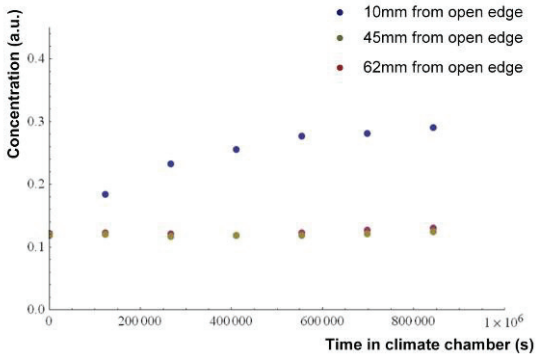

Figure 4: Example of FTIR ratio plotted as a function of time in climate chamber for points at 1cm, 4.5cm and 6.2cm from open edge.

3.3 Contactless Measurement of the Resistivity

The setup is originally calibrated for a small distance between conductive layer and the coil (d~1-2mm). In order to calibrate the setup for a distance which corresponds to the thickness of the glass, sheet resistance of reference samples are measured by the four-point probe method and then measured with the contactless method (see **Figure 5**).

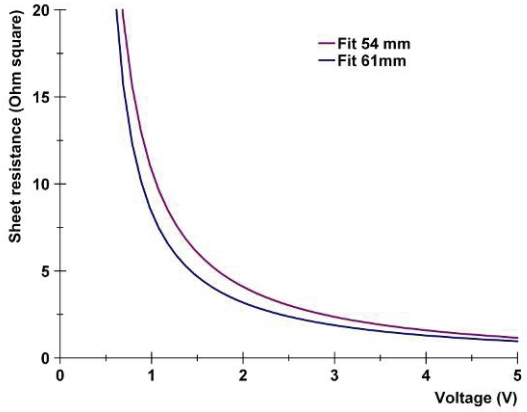

Figure 5: Correlation between voltage from contactless measurement and actual sheet resistance.

After each aging cycle, resistivity is recorded, normalized by the initial value and plotted as a function of distance to the open edge (see **Figure 6**).

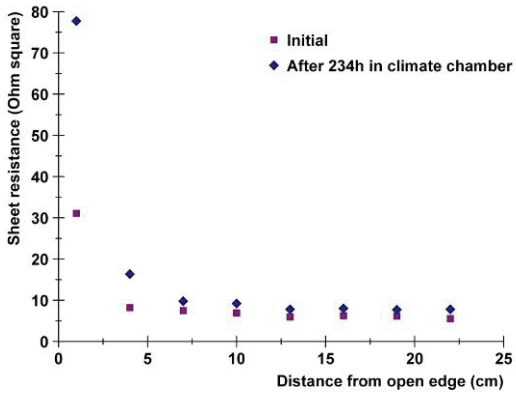

Figure 6: Example of resistivity as a function of distance from open edge, after lamination and after 234h in climate chamber.

Resistivity increases for every point. The increase is more important for points close to the open edge (more than 25% of the initial value). This effect is also observed for samples coated with paint, the points close to the edge being less affected than in non-coated sample (see **Figure 7**).

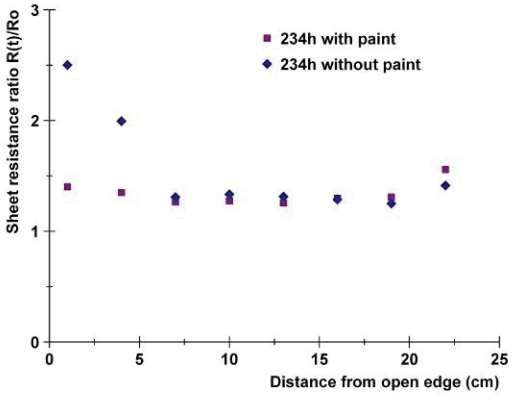

Figure 7: Degradation of conductivity of ZnO is lower in presence of the paint, but the increase of the resistivity of the points far from open edge is the same for both types of samples.

On the other hand, FTIR measurements (see **Figure 3**) seem to indicate that there is no water in the polymer further than 3cm from open edge.

3.4 Diffusion model

Assuming that the diffusion coefficient D in PVB does not depend on water concentration and that the sealed samples can be assimilated to a semi-infinite 1-dimensional media, Fick's law can by used to fit the data and deduce the diffusion coefficient D [8].

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{Fick's law}$$

This law can also be written as [9]:

$$C(x,t) = (C_s - C_i)\left(1 - \mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right) + C_i$$

with

$C = C_i$ at $t = 0$

$C = C_s$ at $t = \infty$

Data were fitted as a function of time in climate chamber (see **Figure 8**), with C_i and C_s set to values inferred from plots. Then a mean value of D was calculated for the points comprised in the first 3cm from open edge. This mean value was used to find a refined mean value for C_s, and finally a refined value for D, $2.10^{-6} \pm 0.4$ cm^2.s^{-1}.

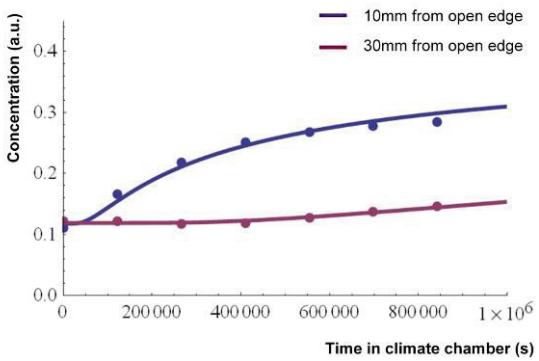

Figure 8: Dots are experimental data and curves are fitting with Fick's law**.**

From this calculated value D, it was observed that the points far from open edge saw the contribution of the sealed edge, even though it was not visible graphically.

4 DISCUSSION

The diffusion equation used to fit FTIR data is valid for a 1-D case that is to say for a big sample or a sample with well sealed edges. In this study, the sealing was not

tight enough as one can see in **Figure 3**. For the calculations, only the few points close to the open edge were taken into account (x small compared to sample size).

Not only sheet resistance widely increases where moisture is present, but it also increases continuously and homogeneously across the samples, whatever the configuration (paint, sealing). By comparing with FTIR data, it seems that this continuous increase is not directly due to water vapour content in the polymer. It is maybe due to an incompatibility with the polymer or to temperature effect.

From the resistance data, it seems that the paint has a protective effect for the ZnO layer whereas edge deletion has no clear influence on it.

A model to correlate moisture content inside polymer to sheet resistance of the ZnO layer as a function of doping is under investigation.

5 CONCLUSION

The present study shows the feasibility of using a non-invasive tool to quantify, with spatial resolution, the electrical degradation of transparent conducting oxide during aging cycle. It is complementary to spectroscopy and permits to study also non-transparent samples.

6 REFERENCES

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